# Quarterly Progress Report

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# FUNDAMENTAL STUDIES OF THE METALLURGICAL, ELECTRICAL, AND OPTICAL PROPERTIES OF GALLIUM PHOSPHIDE

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NATIONAL AERONAUTICS AND SPACE ADMIN LEWIS RESEARCH CENTER CLEVELAND, OHIO

> Work Performed By Solid-State Electronics Laborato Stanford University

Stanford, California

**FACILITY FORM 602** 

PROJECT 5115: SEMICONDUCTOR DEVICES FOR HIGH TEMPERATURE USE

National Aeronautics and Space Administration

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Principal Investigator: G. L. Pearson

Staff: A. J. Domenico

The purpose of this project is to prepare power rectifiers and solar batteries which will operate at temperatures up to  $500^{\circ}$ C. During this quarter, work has commenced on the revised research plan in which the active gallium phosphide layer will be grown by liquid epitaxy.

#### Crystal Growth

As stated in the last quarterly report, a liquid epitaxial layer appears to be advantageous in that it should contain a smaller number of crystal imperfections and should have fewer deep level traps. To provide mechanical support and to provide the crystalline structure upon which to grow the liquid epitaxial layer, a sulfur-doped vapor epitaxial substrate using the method of Hara and Akasaki was proposed. In this method, a secondary stream of sulfur vapor is introduced beyond the gallium source.

The initial attempts to produce the sulfur-doped crystals were unsuccessful. Slightly different operating conditions or slightly different external indications of the operating conditions are probably needed. However, rather than continuing the effort in this direction, a decision was made to use liquid epitaxial techniques to form both the active region and the n<sup>†</sup> substrates. Several advantages accrue from this approach. First, from previous work tin-doped gallium phosphide crystals of carrier concentrations on the order of 10<sup>18</sup> have already been achieved. Secondly, although a supply of single crystal gallium phosphide would be required, the crystalline quality and the doping characteristics are not of overwhelming importance. In regard to the former, the work of Nygren<sup>1</sup> under this contract has demonstrated that liquid epitaxial layers grown on the {111}P face of a seed are of superior crystalline quality to the original seed material. The doping characteristic of the seed is of lesser importance due to the

fact that the only function of the seed is to provide nucleation of the liquid layer, with the seed later removed by lapping. Finally since the requirements are less stringent, gallium phosphide crystals produced for other purposes in this laboratory or produced by other laboratories may be used.

#### Results

For use as n<sup>+</sup> substrates, three crystals were grown in the conventional liquid epitaxial horizontal system. The seeds for these substrates consisted of one vapor-grown sample kindly supplied by S. Nygren and two vapor-grown samples produced last quarter on this project. The liquid epitaxial layers were grown on the {111}P face from an initial temperature of 1050°C and at a cooling rate of 0.32°C/min for 16 hours in a hydrogen atmosphere. The solution contained 10 atom percent tin. The resulting layers ranged from 100 to 275 microns in thickness.

To produce the thin undoped layer of approximately 10 microns thickness, a vertical liquid epitaxial growth was first attempted. The basic vertical system has been described in the quarterly progress report of April 1 to June 30, 1968 and the constructional details are shown in the report of Nygren. For the system actually used, a modification has been incorporated in an attempt to reduce the impurities present. The seed holder consisting of machined graphite together with graphite screws and molybedenum wire has been replaced by one of a new all quartz design.

The first attempt to grow an epitaxial layer failed. The substrate chosen was one of the three n<sup>+</sup> Sn-doped liquid epitaxial substrates previously produced. No noticeable layer was present. A possible reason for the failure could be that the sample was too small to insure that immersion actually occurred upon the lowering of the seed holder. Since most GaP crystals then available were of similar size another supply was needed. The IBM Research Center at Yorktown Heights, New York, has kindly given to us five GaP crystals approximately 10 mm in diameter and 0.5 mm thick. These crystals were grown by the two-

zone vertical Bridgeman method<sup>3</sup> and are tellurium doped with a carrier concentration of approximately  $2 \times 10^{17}$  cm<sup>-3</sup>.

A part of one of the Te-doped samples was used in a second attempt to grow a 10 micron layer with the vertical system. In the resultant crystal the quality of the {111}P face was poor with a large drop of gallium adhering to the surface. The {111}Ga face was therefore considered although the planarity of the seed-layer interface is typically inferior on this side. In fact an examination of one cross-section of the seed did not reveal a layered growth on the {111}Ga face. To confirm this observation, Schottky diodes were constructed by the vacuum deposition of Ni-Ge for the ohmic contact and Cr for the Schottky barrier. The results indicated that the carrier concentration was that of the substrate and that the reverse breakdown was on the order of a few volts as would be expected. Possible causes for the lack of growth include incomplete saturation of the gallium solution with gallium phosphide and the etching of the growth in the hydrogen atmosphere used.

## Plans for Next Quarter

Further work will be continued with both vertical and horizontal liquid epitaxial systems. In particular, effort will be concentrated on the growth of the thin uniform layer in the vertical system.

## References

- 1. S. F. Nygren, "Preparation and Properties of P-N Junctions in Gallium Phosphide," Technical Report No. 5112-3, Stanford Electronics Laboratories, October 1968.
- 2. S. F. Nygren, "Preparation and Properties of P-N Junctions in Gallium Phosphide," Technical Report No. 5112-3, Stanford Electronics Laboratories, October 1968.
- 3. S. E. Blum and R. J. Chicotka, J. Electrochem. Soc. <u>115</u>, 298 (1968).

PROJECT 5116: DONOR IMPURITIES IN GaP

 ${\tt National\ Aeronautics\ and\ Space\ Administration}$ 

Grant NGR-05-020-043

Principal Investigator: G. L. Pearson

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The purpose of this project is to study the behavior of shallow donors in gallium phosphide. In particular, S, Se and Te will be diffused into GaP to determine solubility and diffusion parameters. This information will be useful in delineating the properties of GaP doped with these shallow donor impurities.

This project is being written up as a final technical report and when completed will serve as a quarterly report for Project 5116.